SYNTHETIC DETERGENTS: SOME ASPECTS OF THEIR RELATION TO AGRICULTURE

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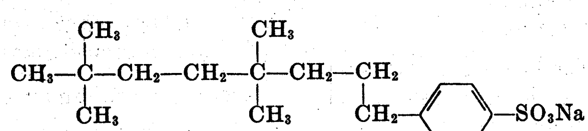
Any cleansing agent is, by definition, a detergent. In this sense, many different kinds of materials would be so classed. For a long time soaps, which are salts of fatty acids, were the detergents most extensively used, but by the end of World War II synthetic detergents made from petroleum products had begun to be produced commercially.

The formulas for a typical soap and a synthetic detergent are as follows:

$$CH_3(CH_2)_{16}C(=O)-O-Na$$

SODIUM STEARATE



SODIUM ALKYLBENZENESULFONATE (ABS)

Both these compounds have a hydrophilic or water-loving polar group, and a hydrophobic or water-repelling group, the aliphatic and aromatic hydrocarbon chain. It is to this dual nature of the molecules that such compounds owe their detergent properties.

Although the detergent properties of these compounds may be approximately equal in soft water, their behavior in hard water is quite different. Soaps are precipitated by the alkali earth metal salts, mainly calcium and magnesium, found in hard water. These precipitates are difficult to remove from cloth, washing utensils, and other products, and it is largely because of the behavior of soaps in hard water that the synthetic detergents, which do not form these insoluble salts, are so much preferred.

Since the introduction of synthetic detergents in commerce they have taken an ever-increasing portion of the market. Figure 1 summarizes these trends in the United States since 1940. The detergent formulations contain only about 25 per cent active detergent, and polyphosphates, sulfates, and other ingredients as builders. With the use of soap decreasing from about 4 billion pounds in 1945 to about 1 billion pounds in 1963, there has been a large accumulation of the animal fats formerly used for soap manufacture. Many excellent fat-based detergents have been synthesized as a possible use for these excess fats.

The classification of surface active agents is based mainly on their electrolytic dissociation. Thus, depending on the nature of the polar grouping, a distinction is made between the anionics, the cationics, and the nonionics.

The following are typical anionic detergents:

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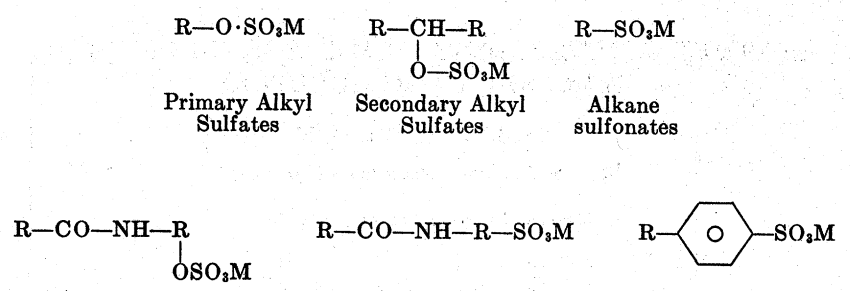
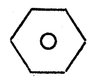


Primary Alkyl Sulfates — Secondary Alkyl Sulfates — Alkane sulfonates

Fatty Amide Sulfates — Sulfonated Fatty Amides — Alkyl Aryl Sulfonates

R = carbon hydrogen chains  aromatic nuclei M = cation

Although representatives of all these types are used, the alkl aryl sulfonates, specifically the many isomers of alkylbenzenesulfonate (ABS), constitute the bulk of the material in common use.

Many typical cationic detergents, represented by the following formula, are quaternary ammonium compounds:

$$\left[\begin{array}{ccc} & \mathrm{R_1} & \\ & | & \\ \mathrm{R_4}— & \mathrm{N} & —\mathrm{R_2} \\ & | & \\ & \mathrm{R_3} & \end{array}\right]^{+} \mathrm{X}^{-}$$

R_1—R_2—R_3—often straight chains
R_4—often an aromatic ring
X—a halogen or any acid

Because of their antimicrobial activity they are used in special antiseptic cleaners, dish-washing compounds, and other cleaning products.

The nonionics result from polymerization of several ethylene oxide molecules on a substance with an active hydrogen. In this example, an alcohol reacts successively with *n* molecules of ethylene oxide to form a new polyoxyethylene alcohol:

$$\mathrm{R{—}OH} + n\underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{CH_2{—}CH_2}} \rightarrow \mathrm{R{—}O{—}(CH_2{—}CH_2{—}O)_{n-1}{—}CH_2{—}CH_2OH}$$

R = carbon-hydrogen chains

These polyoxyethylene chains may react with fatty acids, fatty alcohols, alkylphenols, amines, fatty amides, etc.

The approximate percentage breakdown of the different types of detergents used in several countries is shown in table 1.

The alkyl aryl sulfonates account for approximately four-fifths of the detergents of the anionic type (41), and contamination of water and soil by synthetic detergents is primarily due to these anionic detergents.

NEED FOR BIODEGRADABLE DETERGENTS

With the increased use of synthetic detergents certain problems arose. Certainly the most noticeable of these is the foaming in sewage disposal plants, on rivers and streams, and even at faucets in some areas. Foaming has been so extensive in some places that it has become a hindrance to navigation and a health hazard. In addition to the blowing about the countryside of contaminated foam from sewage treatment plants, ABS is said to reduce settling, reduce oxygen transfer and dissolution, and even inhibit oxidation (38).

STUDIES OF DETERGENT BIODEGRADABILITY

The presence in some areas of ABS in the effluents of sewage disposal plants, in rivers and streams, and in the ground water has been verified. The resistance of these compounds to attack by microorganisms has been studied in some detail. Early workers observed the facility with which alkyl sulfates, in comparison with alkyl aryl sulfonates, degraded. Much of this early work is, however, of questionable reliability, due to the uncertainty both of the methods of analysis and of the physical phenomena involved, particularly adsorption. This largely explains the differences to be found in the rates of biological degradability quoted in the early literature. By the use of radioactive tracers it has been well established that ABS is attacked

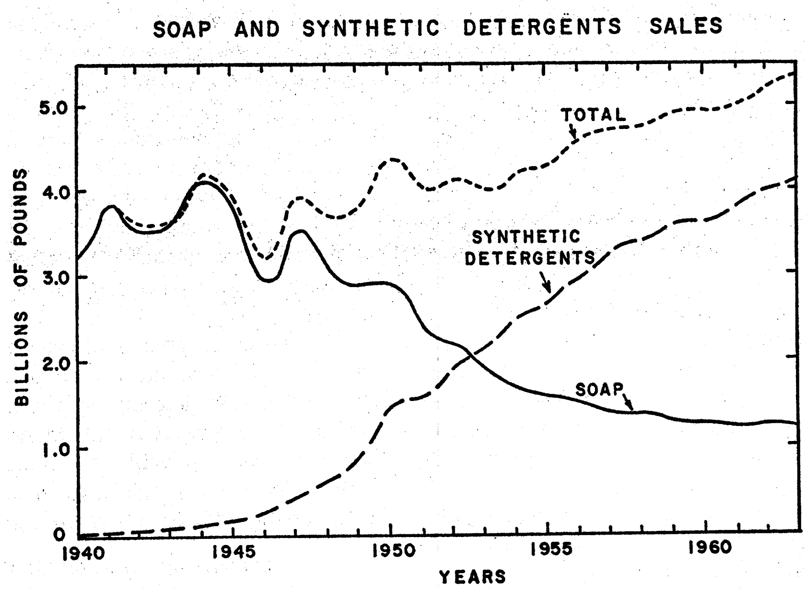


FIG. 1. Soap and synthetic detergent sales in the U. S. (10)

by bacteria, even by the bacteria most usually found in soil or in sewage treatment works, but there are great variations, depending on the molecular configuration, in the rate of attack. Commercial ABS is obtained by condensation of olefins (tetrapropylene) on an aromatic nucleus, followed by sulfonation. The tetrapropylene chain already includes a large number of isomers and, in addition, the commercial product is in reality a mixture of C9 to C15 aliphatic side chain hydrocarbons. Swisher (53) has stated that there are 3057 isomers for the C15H23 chain, and about 80,000 different structures are possible by mixing C12 to C15 alkyl chains. Among the alkyl aryl sulfonates obtained with this mixture of olefins, some readily undergo biodegradation whereas others are very resistant. The isomers that are relatively prone to degradation are called "soft," and those that are particularly resistant are called "hard." Bernarde *et al.* (2) reported a stoichiometric relationship between the appearance of inorganic sulfur and the reduction of ABS concentration, as determined by the methylene blue method, thus indicating attack on the sulfonate portion of the molecule. The concensus, however, seems to be that bacterial attack on detergents begins on the terminal carbon of the chain farthest removed from the point of attachment of the benzene nucleus, with the formation of alkylhydroperoxides by the attachment of an oxygen molecule (15, 18). These hydroperoxides are converted into alcohols, the alcohols to aldehydes, and then into carboxylic acids, and the attack on the chain continues by β oxidation (44, 56). The following is a suggested mechanism:

TABLE 1

Use of synthetic detergents in various countries

Country	Use (%)		
	Anionics	Nonionics	Cationics
United States	67.2	29.8	3
France	93	7	0
United Kingdom	92.3	7.2	0.5
Germany	80	15	5
Switzerland	87	13	0
Netherlands	84	15	1
Belgium	85	14	1

FROM: Prat and Girard (38).

$$R—CH_2—CH_2—CH_2—CH_3 \xrightarrow{+O_2} R—CH_2—CH_2—CH_2—CH_2OOH\ (?) \xrightarrow{-H_2O + H_2}$$

$$R—CH_2—CH_2—CH_2—CH_2OH \xrightarrow{-H_2} R—CH_2—CH_2—CH_2—CHO \xrightarrow{-H_2O - H_2}$$

$$R—CH_2—CH_2—CH_2—COOH \rightarrow \beta\ \text{Oxidation}$$

Destruction of the molecule, however, is frequently not complete, indicating that the reaction might be stopped by structures containing quaternary carbon atoms which do not possess the hydrogen atoms permitting β oxidation. Recent work by Mohanrao and McKenney (29), however, showed that some microorganisms can degrade certain tertiary linked compounds, indicating that the quaternary carbon is not a complete metabolic block. The position of the quarternary carbon in the molecule seems to be a factor.

The influence of the structure of the alkyl chain on the biodegradability of ABS has been studied, using compounds of known molecular structure. As a result of such studies the following conclusions were reached:

(*a*) ABS with unbranched alkyl chains and a benzene ring at the end of the chain are completely biodegradable (30, 43, 45).

(*b*) One or two methyl groups on the carbon adjacent to the phenyl group do not adversely affect biological degradability (30).

(*c*) A quaternary C at the end of the chain strongly inhibits biological degradation (30).

(*d*) A quaternary C near the benzenesulfonic acid group does not appreciably reduce biological degradation.

(*e*) Compounds containing highly branched alkyl chains are resistant to biodegradation.

By using gas liquid chromatography workers have been able to analyze known mixtures of desulfonated ABS isomers. Allred and co-workers (15) prepared isomers with 6, 8, 10, and 12 carbon atoms in the chains and with the phenyl group in various positions and subjected them to attack by bacteria. They concluded that the rate at which alkylbenzenes are oxidized by microorganisms is related inversely to the distance between the terminal alkyl-methyl group and the point of benzene ring attachment. When this distance is 5 carbons or less, the oxidation rate is markedly reduced. Swisher (50) investigated the biological degradability of a mixture of 12 isomers of diheptylbenzenesulfonate (6 para and 6 meta). A thorough analytical investigation, involving the determination of undegraded ABS on activated carbon, and gas phase chromatography after desulfonation before and after exposure to microorganisms, led to conclusions similar to those reached by Allred; the nearer the point of attachment to the center of the chains the more resistant is the diheptylbenzenesulfonate. Swisher also found that generally the meta derivatives are more readily attacked than the corresponding para derivatives and concluded that the ABS becomes more prone to biological degradation as the distance between the terminal C and the sulfonic acid group increases (it should be noted that the distance is greater in meta derivatives than it is in the corresponding para derivatives).

Thus the evidence seems conclusive that the molecular configuration of detergents is one important factor in determining the rate at which they can be degraded by microorganisms. Furthermore, it is possible to prepare straight chain ABS isomers that are relatively easily biodegradable (16, 20, 39, 47, 51, and footnote[2]).

CONDITIONS OF SEWAGE DISPOSAL

There is another factor of great importance that most of these investigators have failed to consider, namely, the various conditions of sewage disposal. Most of these degradation studies were conducted under conditions where oxygen was present, but when the actual conditions of sewage disposal are examined, it is found that very often aerobic conditions do not prevail. In the United States the approximate percentage of sewage that is subjected to each of the types of sewage treatment employed is as follows: no treatment, 18 per cent; primary treatment (settling only), 26 per cent; secondary treatment (activated sludge), 36 per cent; and septic tanks, 20 per cent (55). In 1960, 21 per cent of 109 million people living in metropolitan areas were relying on septic tanks for sewage disposal. Klein and McGauhey (21) give a figure of 30 million people using septic tanks in 1964. Cesspools and septic tanks are designed to be anaerobic (49) and drainage fields may become anaerobic, also. Under poor drainage conditions aerobic bacteria growing on the organic matter may quickly deplete the oxygen supply.

It is difficult to estimate what proportion of our waste water reaches our rivers and seas without prior treatment, but an increasing

[2] "Biological Properties of Surface-Active Material." A paper presented by Dr. Bock at the Fourth International Congress on Surface-Active Substances, September 7–12, 1964, at Brussels.

amount is being held in lagoons or ponds as the primary or sole method of treatment. Porges (38) states that a total of 1304 stabilization ponds currently are used as the principal method of sewage treatment for 2,138,085 of our population; in addition, 827 industrial ponds by 31 industries in 44 states are indicated. Some of these are so-called high-rate oxidation ponds that are shallow in depth and are kept aerobic by agitation to promote growth of algae for oxygenation (32). Others are maintained in an anaerobic condition (14), and still others are designed to cycle between anaerobic and aerobic conditions (9). Porges (37) states that practically all ponds have zones of aerobiosis and anaerobiosis. It seems clear, then, that even in some sewage systems that we usually consider to be supplied with oxygen, anaerobic conditions may and do exist.

Activated sludge sewage disposal plants employ aeration for treating the soluble components of sewage, but the settleable solids as well as the solids produced in the aerated phase are held in anaerobic digesters. The point to be emphasized is that in the biodegradation of detergents their behavior under anaerobic as well as aerobic conditions must be considered.

Biodegradability of Fat-Based Detergents

As pointed out earlier, the use of tallow-based detergents would help solve a pressing agricultural problem. The biodegradation of several of these compounds has been tested under conditions encountered in sewage disposal systems. In the so-called river die-away test the detergent under investigation is placed in water from a local stream. This water is then allowed to

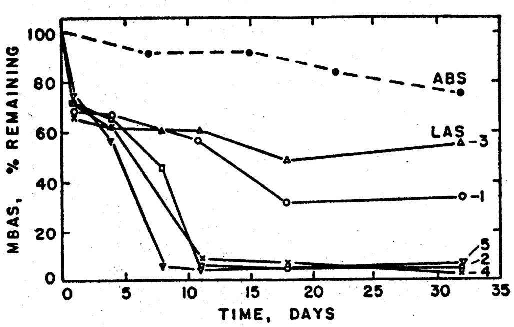


FIG. 2. Biodegradation of LAS in river die-away test (42); MBAS = methylene blue active substance.

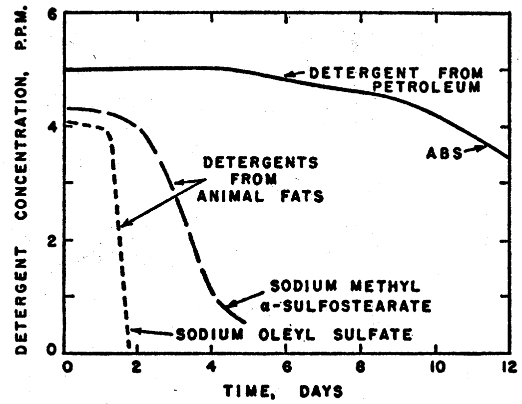


FIG. 3. Biodegradation of detergents from animal fats in river water die-away test.

stand, and at frequent intervals, over a period of several days or weeks if necessary, the amount of detergent remaining in the water is determined. Weil and Stirton (58) screened 33 anionic and six nonionic detergents by this procedure. All fat-derived compounds without mid-chain substitution were found to degrade in Schuylkill River water at 20°C. in less than one week. The most easily degradable compounds were the alkyl sulfates, esters, and amides. The alkanesulfonates, the α-sulfo fatty acids and salts, and the esters of α-sulfo fatty acids were not quite as easily degraded as the compounds in the previously mentioned group. There was considerable variation in biodegradability of the samples of linear alkylbenzenesulfonates (LAS) tested. Some were about as degradable as the alkanesulfonates, whereas others were almost as "hard" as the branched chain ABS. Renn *et al.* (39) obtained similar results, as shown in figure 2. Figure 3 shows a comparison of some representative results from the use of fat-based compounds and petroleum-based compounds.

In another series of tests (8) tallow-based compounds were subjected to conditions similar to those found in an activated sludge sewage disposal plant. A diagram of the unit used, devised by Ludzack (24), is shown in figure 4. These tests were started with sludge from a sewage disposal plant and the aerators were fed continuously with a weak suspension of trout chow containing the detergent under test. They were aerated continuously and the effluents analyzed daily for undegraded detergent.

The bar graph in figure 5 compares the re-

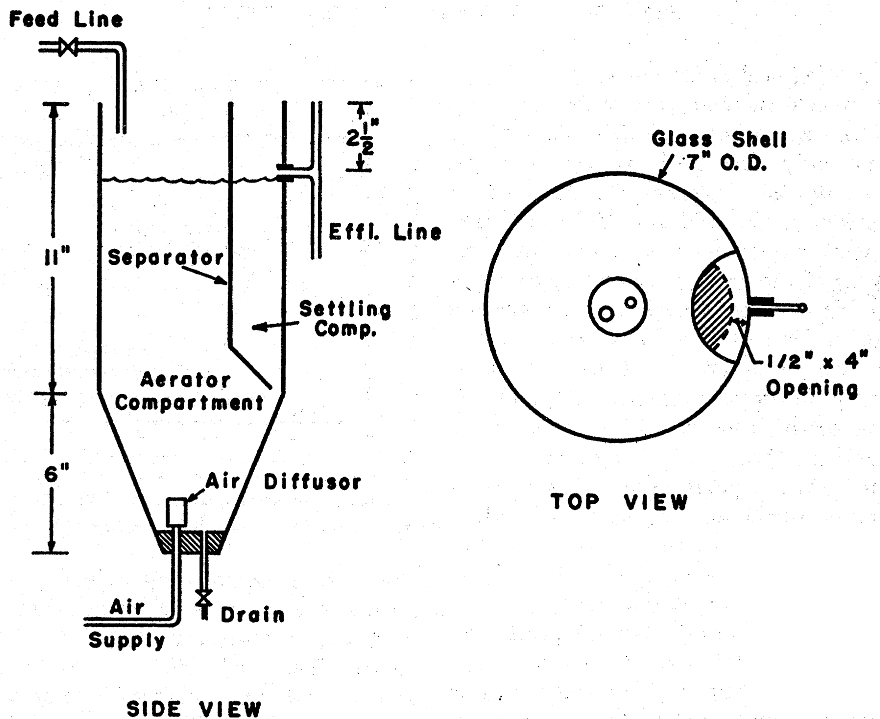


FIG. 4. Model activated sludge unit (24): (*side view*) 7-inch O.D. Pyrex Shell ⅜-inch wall drawn to a cone. (Corning Glass Works, Special App. Div. Reference No. D459051-T140); (*top view*) Separator made from a 10-foot section of 4-inch plexiglass tube cut in half longitudinally; bottom end cut at a 60° angle. Part of the lower end is closed by ⅛-inch plexiglass plate, so that the two compartments are connected by ½ x 4-inch opening. Waterproof "rubber to metal" cement is used to join plexiglass to glass.

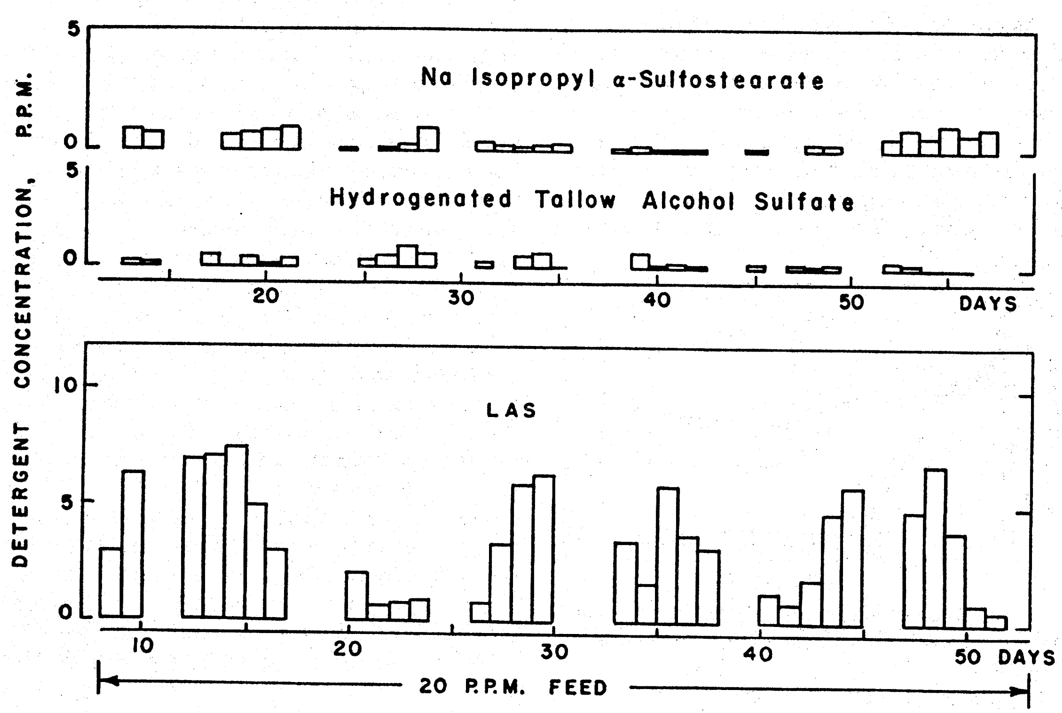


FIG. 5. Degradation of fat-based detergents and LAS in activated sludge (8)

sults obtained with two experimental detergents and LAS. Both tallow-based compounds were almost completely degraded, whereas LAS remained undegraded to the extent of 25 to 60 per cent.

A summary of the results obtained in the river water and activated sludge tests is shown in table 2. It is quite evident that the detergents derived from fats, without mid-chain substitution, were more easily degraded than even the soft LAS materials in these tests.

TABLE 2

Summary of detergent degradation in activated sludge and river water

Detergent	Activated Sludge			River Water
	Average Analyses	High Value	Time Over 1 ppm.	Time for 80% Degradation
	ppm.		%	*hr.*
Sodium oleyl sulfate	0.03	0.3	0	26
Tallow alcohol sulfates	0.4	1.3	3	56
Sodium 9,10-dichlorooctadecyl sulfate	0.2	1.0	0	82
Sodium methyl α-sulfostearate	0.3	1.8	10	93
Sodium isopropyl α-sulfostearate	0.5	1.4	6	117
Disodium 2-sulfoethyl α-sulfostearate	0.7	5.1	17	123
Sodium hexyl α-sulfopelargonate	5.7	19.8	77	265
Disodium α,α-dioctylsulfoacetate	1.6	3.6	65	408
Linear dodecylbenzenesulfonate, LBS I (commercial)	7.3	12.2	100	88
Sodium dodecylbenzenesulfonate, LBS II	3.5	7.4	74	130
Branched alkylbenzenesulfonate, ABS	11.0	17.0	100	>700

FROM: Cordon *et al.* (7).

SYNTHETIC DETERGENTS IN ANAEROBIC SEWAGE DISPOSAL

The behavior of synthetic detergents under anaerobic conditions has received comparatively little attention. Bloodgood and his associates (12, 17) found that when ABS was added to digesting primary sludge (that is, settled raw sewage plus solids from the activated sludge process) so that the concentration was 3.3 mg./g. of total solids, serious disruption of the digestion ensued. Klein (19) found that 750 mg./l. of ABS was near the tolerance threshold in sludge digestion. Wayman, Robertson, and Hall (54) tested the degradation of LAS in sewage effluent under anaerobic conditions and concluded that significant amounts could not be degraded in the temperature range of 10°–35°C. Brink[3] stated that neither LAS nor ABS can be biodegraded under anaerobic conditions.

Klein and McGauhey (20) followed radioactive labeled LAS through a simulated septic tank-percolation field. Some of their results are shown in table 3. Very little degradation of detergent LAS took place in the septic tank but almost all was degraded in the percolation field. It is interesting that 60.8 per cent of the alcohol sulfate was removed in the septic tank where anaerobic conditions prevailed. This study by Klein and McGauhey was extended to include conditions where the percolation field was flooded. LAS and alcohol sulfate were removed to almost exactly the same extent as before but the removal of ABS decreased significantly. By flooding, anaerobic conditions were produced in the bottom of the trench but oxygen was always present in the surface water. Under these conditions, a much larger proportion of the detergent was removed by adsorption, but the detergent that escaped adsorption was readily degraded even when the dissolved oxygen was drastically reduced. It seems likely, however, that under actual use conditions the oxygen would become completely used up, in which case LAS detergents would presumably not be degraded.

Maurer *et al.* (26) subjected tallow-based detergents to conditions in a system simulating those found in the anaerobic phase of a sewage disposal plant. The gas evolved (mostly methane) was collected and measured. Figure 6 shows the course of the gas evolution. The ABS and LAS samples caused gas evolution to stop when the concentration of added detergent reached about 250 mg./l. One of the fat-based detergents also became toxic to the system but at a much higher concentration. In the case of the other tallow-based detergents, gas evolution equaled or exceeded that of the control.

The amount of detergent present after 30 days incubation is shown in table 4. Only two compounds degraded, the tallow alcohol sul-

[3] Personal communication from Robert Brink, Atlantic Refining Company, Philadelphia, Pennsylvania.

TABLE 3

Summary of detergent degradation and removal

Results	Algal Growth Units			Oxidation Ponds			Septic Tank			Septic Tank and Percolation Field*		
	PP	SC	ALC	PP	SC	ALC	PP	SC	ALC	PP	SC	ALC
	%											
Detergent degradation	2.9	35.3	94.2	15.9	80.5	93.7	3.8	−0.7	20.9	60.5	87.3	54.3
Degradation to sulfate	1.6	5.5	—	0.8	11.8	—	−0.5	−1.1	—	29.9	70.0	—
Percolation field, detergent removal efficiency	—	—	—	—	—	—	—	—	—	74.1	97.1	98.8
Detergent removal	<15.0†	56.2	95.2	<40.0‡	93.1	98.0	16.3	9.6	60.8	78.2	96.9	99.6

FROM: Klein and McGauhey (20).

PP = polypropyl ABS; SC = straight chain ABS; ALC = alcohol sulfate.

* Calculations based on influent to septic tank and therefore refer to entire septic-tank percolation-field system. The exception is the removal efficiency in the percolation field, which is based on the influent to the percolation field.

† System did not reach steady state; detergent removal less than 15 per cent.

‡ System did not reach steady state; detergent removal less than 40 per cent.

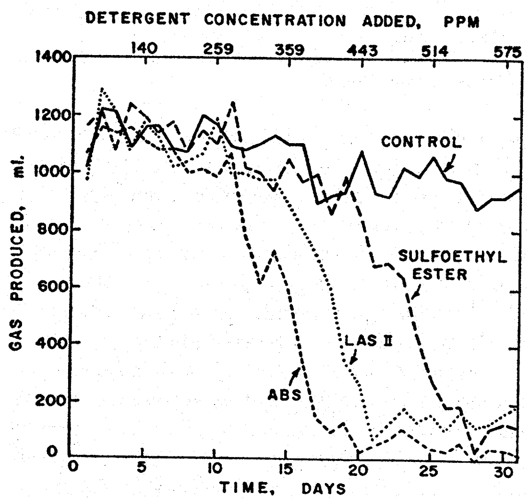


FIG. 6. Daily gas production from anaerobic digesters containing detergents (26).

fates HTAS and Na 9,10-dichlorooctadecyl sulfate. The other tallow-based compounds did not degrade, but, with the one exception noted, they were not toxic to the system as were the petroleum-based products.

CONTAMINATION OF SOILS BY DETERGENTS

Before discussing the consequences of contamination of soil by detergents it might be well to consider how this contamination can take place. It appears that the largest source of contamination by detergents would be through contaminated ground water. Ground water can be contaminated by seepage from cesspools and absorption fields used for disposal of household sewage, oxidation ponds for treatment of municipal sewage, natural and induced infiltration from streams or channels receiving sewage, holding ponds for industrial and commercial wastes, and facilities for waste disposal from commercial laundries (52). Such contamination represents a problem of increasing magnitude, especially in metropolitan fringe areas.

Sewage sludge used as soil conditioner would also be an important source of contamination. Digested sludge may contain 800 ppm. or more of ABS. Some surfactants reach the soil because they are components of plant-treating formulations, and finally water-containing detergents (sewage plant effluents, for example) may be used for irrigation, or may be applied to soil as a means of water purification. This has been practiced on a large scale in Australia (34). Pennsylvania State University[4] has a project under way at the present time to test this latter possibility. The Los Angeles County

[4] Personal communication from M. A. Farrell.

Sanitation districts have initiated a water conservation system whereby the effluent from an activated sludge sewage disposal plant is returned to the ground water system (35). The ABS content of the effluent is reduced from about 3.5 ppm. to about 1.8 ppm. by foam separation. The demonstration plant at Whittier Narrows successfully processes 12 million gallons per day.

EFFECT OF SOILS ON DETERGENTS

The problem of the interaction of detergents with soils has been investigated more perhaps from the standpoint of what happens to the detergents in contact with soil than the converse—what happens to the soil. Robeck, Bryant, and Woodward (40) found no significant breakdown of ABS in water-saturated soils; Page, Wayman, and Robertson obtained similar results (33). In unsaturated soils, however, much ABS was removed.

TABLE 4

Detergent concentration for each digester, after 30 additions of detergent

Digester	Detergent Concentration Added ml./l. (ppm.)	Found	Corrected
Control	—	229*	0
LAS I	563	842	613
Na isopropyl α-sulfostearate	563	815	586
Control	—	265*	0
ABS	563	852	587
Na methyl α-sulfostearate	563	804	539
Na_2 2-sulfoethyl α-sulfostearate	563	890	625†
HTAS	563	265	0
Control	—	280*	0
LAS II	575‡	853	573
Na 9,10-dichlorooctadecyl sulfate	575‡	301	21

FROM: Maurer *et al.* (26).

* Calculated as ABS.

† High value because of di-ionic nature of disodium 2-sulfoethyl α-sulfostearate.

‡ Milligrams per liter added for 31 days. Because stored samples gave very erratic results the addition of detergent was extended here so that analysis could be made on a workday.

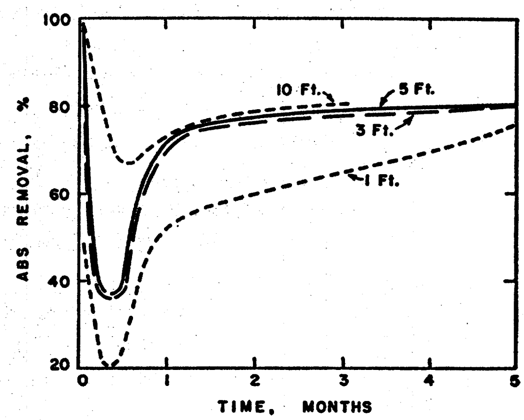


FIG. 7. ABS removal *vs.* depth in soil lysimeters (2).

Bendixen, Robeck, and Woodward[5] investigated the relation of the removal of COD, NH_3-N, and ABS to depth, hydraulic load, and effective particle size. ABS removal *vs.* depth is plotted in figure 7. From such data it was concluded that increased depth of an unsaturated soil zone above a water table in Ottawa sand lysimeters improves their treatment potential. After 5 months of operation, Ottawa sand lysimeters, following an initial lag in treatment, were removing 70 to 80 per cent of the ABS, 70 to 90 per cent of the COD, and 90 to 100 per cent of the NH_3-N that was applied in septic tank effluents.

An extension of this work by Cohen, Robeck, and Woodward[6], using ABS tagged with radioactive sulfur, showed (fig. 8) that in a mature lysimeter only about 2 to 3 per cent of added ABS came through undegraded. Nineteen to 26 per cent was present as degradation products, that is short carbon-chained benzenesulfonates, and 71 to 79 per cent was completely oxidized to inorganic sulfate. In immature lysimeters conversion was not so complete; 35 to 56 per cent of the ABS remained unchanged, and only 1 to 11 per cent was completely oxidized.

[5] "The Use of Soil for Liquid Waste Disposal and Treatment." A paper by T. W. Bendixen, G. G. Robeck, and R. L. Woodward presented at the American Chemical Society Waste Water Renovation Symposium, Cincinnati, Ohio, January 14, 1963.

[6] See footnote to table 6.

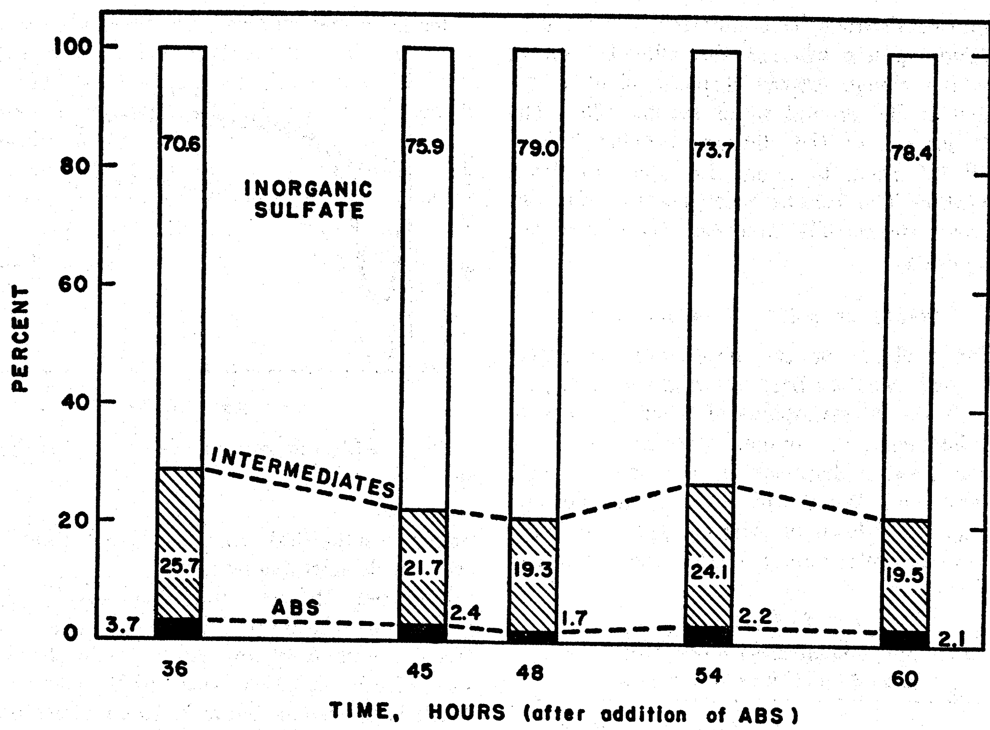


FIG. 8. Composition of effluents from mature lysimeter (see "Degradation of ABS in Unsaturated Soils," in footnote to table 5).

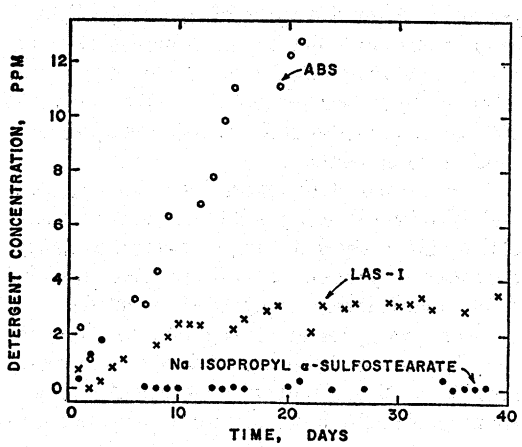


FIG. 9. Detergent analysis of lysimeter effluents (26).

No reports have been noted of extensive studies of this nature in which soft, LAS-type compounds have been tested, but some preliminary lysimeter tests (fig. 9) were conducted in our laboratory using a Califon silt loam soil (26). Effluent analysis by the methylene blue procedure showed 35 per cent degradation of ABS, 83 per cent of LAS, and 100 per cent degradation of sodium isopropyl α-sulfostearate, a tallow-based detergent.

Absorption of surface active agents by soil and clay minerals has been studied by several investigators. The results of Cohen *et al.*[7] (table 5) show that sand and sandy soils absorb comparatively little ABS, whereas clays, with relatively large specific surface areas, absorb much more, but still only 55 to 65 μg. of ABS per gram. A more significant factor in absorption is suggested by the data shown for the cold frame soil, where a value of 252 μg. of ABS per gram of soil was obtained. The high capacity of this predominantly clay soil was due to its high content (25 per cent) of organic matter. The importance of organic matter in the absorption capacity for ABS is shown (table 6) by analyses on soils removed from various depths in the lysimeters after long periods of operation. In many instances the ABS content of the soil was much greater than its original

[7] *Ibid.*

TABLE 5

Adsorption of ABS on soils and clay minerals

Soil or Clay Mineral	Organic Matter (%)	Adsorption Capacity (μg. ABS/g.)	Specific Surface Area $m.^2/g.$
Ottawa—sand	0.08	2.4	—
Chillicothe—sand	0.06	2.7	0.005
Newtown—sandy soil	0.34	11.1	0.01
Long Island—sandy soil	0.02	7.3	0.16
Kaolinite—clay mineral	<0.02	65	5.5
Montmorillinite—clay mineral	0.02	55	5.4
Cold frame—composted clay soil	25	252	—*

FROM: "Degradation of ABS in Unsaturated Soils." A paper by J. M. Cohen, G. G. Robeck, and R. L. Woodward presented at the 129th Annual Meeting of the American Association for the Advancement of Science, December 27, 1962, Philadelphia, Pa.

* Organic matter interfered with analysis.

adsorption capacity for ABS. This increase was undoubtedly due to the organic matter, which provided the additional surface area. Bower and Geschwend (4) reported that organic matter increased the apparent surface area of soil by 558 to 803 $m.^2$ per gram of organic matter. Rotini and Galoppini (41) found the adsorption of sodium dioctyl sulfosuccinate by different soils to be in the following increasing order: sandy, organic-sandy, clayey-calcareous, clayey, peaty. In general, this is in agreement with the results just cited.

Wayman and coworkers studied the adsorption of ABS on various soil minerals (53). They found that adsorption increases with increase in concentration of ABS and the number of carbon atoms in the alkyl chains for the types studied (C12 and C15); apparently the free energy of adsorption increases with increase in molecular weight. For all conditions studied, adsorption attains a maximum value at pH 4 as compared to either pH 7 or pH 10; the acid range no doubt creates significant numbers of positive sites on the clay surface, which are conducive to anionic ABS removal. When phosphate or carboxymethylcellulose are in solution with ABS, these anions do not compete with ABS for adsorption sites. Some unknown mechanisms that aid in the fixation of phosphate on clays seem to enhance ABS removal when both are in solution. When salts are in solution with ABS, the removal of ABS by clays is increased; this effect is most obvious in acid solution (pH 4) and increases as salt concentration increases to about 1000 ppm., beyond which adsorption decreases with increase in salt concentration. ABS adsorption on clays is generally favored by highly charged ionic salts; that is $Al^{+++} > Ca^{++} > Na^{+}$. Several complex physicochemical phenomena must be considered to explain ABS adsorption in the presence of ionic salts.

Figure 10 shows the inefficiency of clay minerals in comparison to synthetic adsorbents. Because most natural waste water has a pH near seven, it seems obvious from these studies that clay minerals cannot absorb significant amounts of ABS; this fact, therefore, partially explains the pollution of ground water from ABS. Klein and McGauhey (21), using radio-

TABLE 6

ABS and organic matter content of soils from lysimeters

Adsorbed ABS*	Organic Matter
μg. ABS/g.	*% dry weight*
Col. No. 1	
7.6	0.25
60	0.63
105	1.06
Col. No. 4	
6.0	0.26
92	1.9
Col. No. 5	
8.8	0.36
115	1.18
148	1.49

FROM: "Degradation of ABS in Unsaturated Soils." A paper by J. M. Cohen, G. G. Robeck, and R. L. Woodward presented at the 129th Annual Meeting of the American Association for the Advancement of Science, December 27, 1962, Philadelphia, Pa.

* Original adsorption capacity of Newtown soil was 11 μg. ABS/g.

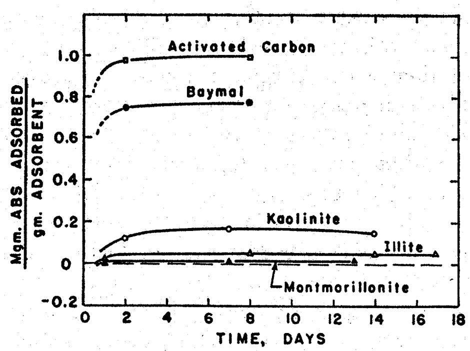


FIG. 10. ABS adsorption of clay minerals compared to that of synthetic adsorbents (57): (*open square*) activated carbon and 10 ppm. ABS, pH = 7; (*solid circle*) baymal and 10 ppm. ABS, pH = 4; (*open circle*) kaolinite and 10 ppm. ABS, pH = 4; (*open triangle*) illite and 5 ppm. ABS, pH = 4; (*solid triangle*) montmorillonite and 4 ppm. ABS, pH = 4; all ABS is dodecyl type.

active ABS (32), found that all soils examined displayed an ability to absorb ABS, but there was an early breakthrough of ABS (32), the more permeable soils (least adsorptive) requiring the shortest period of time. The ratio of effluent to influent ABS reached 90 per cent in about half the time required for 100 per cent breakthrough.

EFFECT OF DETERGENTS ON SOILS AND SOIL PROCESSES

Whether adsorbed on soil particles or not, there seems to be little doubt that surface-active agents in the soil or its water can influence soil structure and some of the processes that take place therein. As early as 1949, surface-active agents were applied to soils in attempts to improve their stability (46). Early results indicated that cationic surfactants reduced air-dry strength and improved the rate of slaking of highly plastic fine-grained soils. Soil conditioners were introduced on a commercial basis in 1952. These were either sodium or calcium salts of 28 to 35 per cent hydrolyzed polyacrylonitrile, or carboxylated vinylacetate-maleic acid polymers (Krilium manufactured by Monsanto Chemical Co.). The effect of these compounds on aggregation, aeration, and water relationship in soils has been reported by Hedrick and Mowrey (11). Their effects on the structure of saline and alkaline soils were studied by Allison (1). Martin *et al.* (25) reported on soil and crop responses from field applications of the soil conditioners; their effect on erosion control was studied by Weeks and Colter (57), and their influence on the mechanism of clay aggregation by Ruehrwein and Ward (42). From such studies it is clear that synthetic polyelectrolytes do exert beneficial effects on the physical properties of soils. Increased yields of vegetables from Krilium-treated silt-loam were found by Hedrick and Lowry (11), increased yields of corn, oats, and carrots by Martin *et al.* (25), and corn, on alkali soils, by Allison (1).

Michaels (27) studied the effect of polyacrylamide on soils and found that flocculation can occur by two basically different phenomena: (*a*) the electrokinetic potential of the particle surfaces may be reduced sufficiently to permit particle aggregation and cohesion by residual valence forces; or (*b*) the particles may (if of adequate size) adsorb on more than one particle and thus be directly responsible for interparticle bonding. This latter condition would prevail when the polymer concentration was low. When the polymer concentration was high the bonds of the suspended solids would become saturated by polymer molecules and result in the formation of stable dispersions. When flocculation occurs the particles pack loosely in the soil, improving the water-holding capacity, aeration, friability, resistance to crusting, and erosion. Grossi and Woolsey (10) found that a Putnam silt loam treated with dimethyldioctadecylammonium chloride reaches an apparent limit to the quantity of water adsorbable that is much lower than an untreated soil. This is directly responsible for its hydraulic stability and also explains the ability of the treated soil to withstand rupture from cyclic wetting and drying and also from freezing and thawing.

In 1954 E. A. Clarke of the Atlantic Refining Company was awarded a U. S. Patent (6), "Process for Treating Soil with Alkylbenzenesulfonates." The main claims of this patent were that ABS enhanced the water penetration and retention characteristics of soils and hence stimulated the growth of vegetation. It was claimed that very dilute solutions of ABS could be very effectively used in irrigating or watering humus-deficient soils to improve the contact between water-soluble constituents of natural or commercial fertilizers and the roots of plants. It was suggested that ABS assists water in thoroughly wetting particles of dry soil, root hairs, and the water-soluble nutrients, and provides an efficient and economic method of transfer of nutrients from soil to roots. Treatment of soil with ABS was supposed to so increase water penetration that erosion would be alleviated, and, further, that the water would be so strongly retained that heretofore useless arid and semiarid land would become satisfactory for commercial crop growing. It was also claimed that vegetation irrigated in the presence of ABS required only about a third as much water to prevent wilting as would normally be required with water alone. The possibility was suggested that vast areas of unproductive and highly alkaline soils could be converted into grazing or farming land through frugal irrigation, employing small concentrations of ABS which would decompose eventually into products that would acidify the soil.

Another patent (13) was awarded to S. J. Hetzel of the Sun Oil Company for a process involving the application of green sulfonic acid ammonium salts to soils (prepared by the sulfonation of mineral oil and subsequent preparation of ammonium salts). It was believed these compounds acted as nutrients and also as wetting agents, thus facilitating the movements of water and soluble nutrients through the soil to the plant roots.

In 1957 Seymour (48) reviewed the status of research related to the use and effect of surfactants on various crops and soils. Of fourteen references cited, two were to the patents just reviewed, and two were to a symposium held by the American Society of Agronomy, in Dallas, Texas, in 1953, that does not appear to have been published. The remaining ten citations all referred to unpublished work. Instances were cited of increased yields of some crops, no effect on others, and in one case, a decreased yield (of potatoes) when surfactants were applied to soils. Lemon (23), in considering the potentialities for decreasing evaporation loss from soils, reported on work done by several Russian investigators as well as his own studies. The data presented demonstrate the influence of surfactants on capillary flow in clay-water systems of the montmorillonitic and kaolinitic types. The results indicate that the moisture retentivity of the soil can be increased or decreased, depending upon the surfactant and the type of clay mineral involved.

Permeability is the readiness with which a fluid can pass through a filter. Chavanne (5) has shown that the presence of detergents in sewage increases the flow through filters with a permeability of more than 10^{-4} m./sec., and decreases the flow through those with a permeability of less than 5×10^{-5} m./sec. In addition, detergents leave a deposit on the filter, and the thickness of this deposit increases with the specific surface of the filter, that is with the fineness of the particles. In the case of low permeabilities (less than 10^{-4} m./sec.), the gas bubbles may cause partial "clogging" of the filter. According to Plegat (36) variations in the permeability and porosity of easily worked soils depend in part on the capillary phenomena as the liquid moves between the mineral particles. If the spacing is sufficiently open, the dominant factor will be gravitational flow; conversely, if the distances between the particles are small, most of the liquid moves by capillary action. The capillary effect is then diminished by detergents (in unsaturated soil) and the flow is reduced accordingly. Rotini and Galoppini (41) found an increase in the sedimentation velocity of soil particles in the presence of detergents and a modification of the degree of dispersion. They considered these effects on soil structure to be quite significant.

Mistry and Bloodworth (28) carried out laboratory studies of the effects of nonionic, cationic, anionic, and amphoteric surface-active compounds and long-chain fatty alcohol in suppressing evaporation from coarse-textured agricultural soils. The data obtained indicate that two of the compounds, a nonionic surfactant and a fatty alcohol, were highly effective in reducing water evaporation from a coarse sand. Evaporation from a fine sandy loam soil was retarded effectively by irrigating with water containing a nonionic compound. There was found to be a strong interaction between soil texture and effectiveness of evaporation suppressors. An extension of these studies by Law (22) included the introduction of these controlled variables: treatment rate, relative humidity, and wind velocity. Fatty alcohol, a commercial mixture of hexa- and octadecanol, effectively reduced evaporation from sand surfaces up to a maximum of 87 per cent at 400 pounds per acre, at 20 per cent relative humidity, and at a wind velocity of 2 miles per hour. The greatest reduction with a fine sandy loam soil was 24 per cent at 800 pounds per acre, 20 per cent relative humidity, and at a wind velocity of 2 miles per hour. A nonionic surfactant reduced evaporation from the soil surface up to a maximum of 52 per cent at 60 per cent relative humidity and a wind velocity of 8 miles per hour.

Law postulated that the mechanism by which the fatty alcohol suppressed evaporation from sand appeared to be essentially the same as that which acts to reduce evaporation from an open-water surface. With the soil, however, the mechanism appeared to be that of reducing capillary flow of moisture to the soil surface. The action of the nonionic surfactant in reducing evaporation was probably due to decreased surface tension at the solid-liquid interface, thereby reducing capillary flow to the surface layer of soil and causing the formation of a dry diffusion barrier.

The effect of fatty alcohols on evaporation of water from soil was investigated by Olsen, Wanatabe, Clark, and Kemper (31). The surfactant used was a commercial product that contained 44 per cent cetyl alcohol and 46 per cent stearyl alcohol; the soil was a Weld loam. A cycle of water addition and evaporation for 10-day periods was continued for 14 months. Surface placement of the surfactant resulted in a 43 per cent decrease in water loss in a 10-day period. This effect remained unchanged over the 14-month test period. The mechanism of the action was ascribed to the rapid drying of the surface layer, thus creating a diffusion barrier to water loss by vapor transfer. Fatty alcohol was also found to increase the rate of water infiltration apparently by increasing the stability and size of aggregates.

The effects of detergents on transfer and dissolution of oxygen in aqueous systems, referred to earlier, has been the subject of considerable study. Presumably, many of these actions may operate in soils as well. Detergents have been found to reduce re-aeration, reduce the coefficient of exchange under certain conditions, and encourage the release of oxygen adsorbed on immersed porous bodies. The converging findings of all these investigations clearly show that anionic detergents serve to inhibit and retard oxidation.

Reference has been made to claims of several investigators of beneficial effects of detergents on certain crops. Rotini and Galoppini (41) have found, however, that above a certain concentration detergents exert a considerable anti-mitotic action on onion bulbs. This effect was found with several compounds including alkyl-aryl-sulfonate–based compounds of commerce which were effective *in situ* at 0.025 per cent; considerably more toxic than ordinary soap, which was toxic at 0.1 per cent. The pH was important in determining the anti-mitotic threshold; with sodium lauryl sulfate at pH 7.0 this effect was four times as strong as at pH 6.4. This work was extended to include a study of the effect of these compounds on the germination of wheat, barley, corn, rice, beans, peas, and fesque. A 0.025 per cent solution exerted an inhibitory effect on the pre-prophase of karyokinesis. The inhibitory effect was traced to action on the enzyme systems. It is unlikely, however, that such high concentrations of detergent would often be found under field conditions. A recent study by Bing and Boodley (3) failed to show any adverse effect on the growth of several ornamental greenhouse plants. The plants were watered for 5 months with solutions containing up to 4 ppm. of ABS. Similar results were obtained with radishes.

The statement is often heard that the presence of nondegradable detergents in water systems is advantageous because it calls attention to the gross contamination present. There is certainly an element of truth in this, but on the other hand, the contamination might not have been present except for the presence of the detergent. Although 1 to 10 ppm ABS did not have a significant influence on the movement of coliform organisms through sands saturated with water (40), detergents can affect soil permeability, and it has been suggested that the movement of such agents as viruses, carcinogens, and bacteria through the soil might be facilitated by detergents. It is significant that the Harvard University School of Public Health has recently announced the receipt of a grant from the U. S. Public Health Service to study the transport of pollutants in soils. Dr. Richard L. Woodward[8], who is in

[8] Personal communication.

charge of this work, has stated that their studies will be concerned initially with some rather simple soil, water, salt, and gas systems not involving any significant biological activity. They will be studying gas, water, and salt movement in unsaturated flow. It is hoped that the study being carried out at Pennsylvania State University, already referred to, will also produce information on this subject.

CONCLUSIONS

In conclusion, ABS and the problems associated with its use are still with us. During 1965, however, industry began "voluntarily" changing over to biodegradable, straight chain compounds. Based on laboratory studies and some field studies (39) it is hoped that this change will solve the detergent problem. Tests carried out in England have indicated that this may not occur, even under highly aerobic conditions of sewage treatment[9]. A material that showed 94 per cent degradation in laboratory tests was substituted for the hard ABS detergent throughout most of southern England. Evidence obtained indicated that a complete changeover to the "soft" material over the whole country could lead to a reduction in the concentration of surface-active matter in sewage effluents to about half that observed when only the "hard" detergent was in use, but only when the efficiency of treatment is very high.

Kelly, Konecky, Shewmaker, and Bernheimer[10] tested a linear alkylbenzenesulfonate, a commercial material from Great Britain, in a full-scale sewage plant of the percolating-filter type for about 3 months. Total removal was 34 per cent, but only 27 per cent was actually degraded. The other 7 per cent was adsorbed on the solids. In view of such findings, and especially because of the non-biodegradability under anaerobic conditions, many people believe that the linear ABS will be only a stopgap and that in a few years another generation of detergents will be necessary (59).

In view of the probability that detergents will continue to be added to soils through waste disposal practices, and since surface-active agents do affect soils and processes occurring therein, continued study to clarify these reactions seems amply justified. Furthermore, in view of the water shortage that is facing this country and many other parts of the world, the possibility of conserving soil moisture by the application of surface-active agents has tremendous implications. It appears that increased research in this area might yield rich dividends.

[9] "Detergents and Sewage Treatment; Introduction of Biologically Degradable Materials in Great Britain." A paper by G. A. Truesdale and G. E. Eden presented at the Fourth International Congress on Surface-Active Substances, September 7–12, 1964, at Brussels.

[10] "Physical and Biological Removals of Detergent Actives in a Full-Scale Sewage Plant." Society of Chemical Industry Symposium on Surface Activity and the Microbial Cell, London, September 24, 25, 1964.

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